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(54) **Procedure for the bleaching of pulp.**

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Description

The present invention relates to a procedure for the bleaching of pulp, in which procedure an oxidating bleaching chemical containing chlorine is used.

Especially pulp obtained from a sulphate pulping process is of brown colour, which is mainly due to the lignin remaining in the pulp. Lignin is removed from the pulp by bleaching, which is a process consisting of several stages. During this process, the pulp is treated alternately with oxidizing, lignin-degrading chemicals and chemicals dissolving the degradation products. Oxidizing agents commonly used are oxygen and chlorine-containing chemicals such as pure chlorine gas, chlorine dioxide and sodium and calcium hypochlorites, whereas alkali solutions are used for eliminating the degradation products.

In the reactions occurring in bleaching using chlorine-containing chemicals, lignin is converted into organic chlorine compounds, which are dissolved in the spent bleach liquor. Spent bleach liquors are a problem in regard of environmental protection because of the toxic nature of the chlorophenols and other possible organic chlorine compounds contained in the liquids. Besides, the chemical oxygen demand in spent bleach liquors reaches detrimental levels. As the measures aimed at reducing the environmental pollution load resulting from sulphate pulp production have so far been concentrated on other parts of the process except bleaching, the relative significance of bleaching as a polluting factor has been increasing.

The spent bleach liquors causing the worst environmental pollution load are produced during the washing following the first chlorination and the first alkali treatment in the bleaching process. To reduce the emissions of effluents, various methods have been employed, e.g. the so-called extended digestion, the use of chlorine dioxide as an oxidating bleaching chemical, oxygen bleaching and biological purification of the spent bleach liquor. However, the results achieved by these methods are not completely satisfactory. Although the amounts of chlorophenols and other toxic chlorine compounds in the spent bleach liquor have been significantly reduced by employing chlorine dioxide and oxygen bleaching, it has not been possible to achieve a sufficient reduction in the chemical oxygen demand values of the effluents. Therefore, the methods referred to have required the employment of efficient biological purification.

WO-A-8 908 738 discloses the effect of the enzyme treatment on the reduction of the chlorine content of bleached pulp. In this document it is mentioned that chlorine chemicals are used in the bleach, and example 3 discloses a chlorine dioxide content of 10 percent.

Abstract Bulletin of the Institute of paper chemistry, Vol. 57, No. 7, 1987, page 992, abstr. no. 8912; Int.Cont.Biotechnol.Pulp & Paper Ind. (1986), 67-69 also discloses the use of an enzyme for the reduction of the chlorine content. Here again, however, the chlorine dioxide content used is about as low as it is suggested by the first cited document.

CA-A-1 086 905 discloses a bleaching with a high content of chlorine dioxide, but without any enzyme treatment.

It is the object of the invention to provide a procedure for the bleaching of pulp that enables the toxic content and chemical oxygen demand of the spent bleach liquor to be reduced so as to reduce the need for purification of the liquor.

This object is achieved by the characterizing portion of claim 1.

It has been observed in earlier investigations that by using enzymes it is possible to separate lignin and/or hemicellulose from cellulose and thus give the pulp a more spongy quality. This justifies the assumption that if the pulp obtained from the digestion process is first subjected to enzyme treatment, it is possible to reduce the amount of chemicals used in the next bleaching phase. According to the invention, it has now been observed that enzyme treatment substantially reduces the amount of organic chlorine compounds in the spent bleach liquor while at the same time reducing its chemical oxygen demand, especially when at least 70 % of the bleaching chemical used in the oxidation stage consists of chlorine dioxide. If pure chlorine gas is used, enzyme treatment has a substantially weaker effect on the quality of the spent bleach liquor.

According to the invention, the pulp is subjected to enzyme treatment and washing before the first oxidation stage. The enzyme breaks down hemicellulose and/or lignin contained in the pulp and renders the pulp more spongy, thus enhancing the effect of the chemicals in subsequent oxidation and alkali treatment stages. By washing the pulp after the enzyme treatment, the degradation products are removed and can be burned so that they will not contribute to the effluent emissions at all.

Except for the enzyme treatment, the bleaching of pulp by the procedure of the invention can be performed in the conventional manner by employing alternate oxidation and alkali treatment phases and washing the pulp after each of these phases to remove the bleaching chemicals and degradation products.

The enzyme treatment as taught by the invention is preferably carried out in a temperature range of 10-90 °C, the most suitable range being 40-75 °C, with pH values in the range 3.0-10.0, preferably 4.0-9.0.

The enzyme used can be a hemicellulase, cellulase, pectinase, esterase or a mixture of these.

In the following, the invention is described in greater detail by the aid of examples of embodiments based on laboratory experiments.

Example 1

A diluted enzyme mixture (streptomyces hemicellulase) was added to 220 g of dry matter obtained from birch sulphate pulp (with a dry matter content of 30%) so that a mixture with a consistency of 10% and xylanase activity of 5 U/g of pulp dry matter was obtained. The temperature in the enzyme treatment was 55 °C, the duration of treatment 2 h and pH 8.0.

After the enzyme treatment the pulp was subjected to an oxidating bleaching treatment using a mixture containing 90 % chlorine dioxide and 10 % chlorine gas, in a dosage equal to 1.4 x post-enzyme-treatment kappa number of the pulp. Treatment temperature was 55 °C and duration of treatment 45 min. After the oxidation phase the pulp was washed in a Büchner funnel with a 20-fold amount of water.

Next, the pulp was subjected to an alkali treatment using a 5 % sodium hydroxide solution in a dosage of 0.8 x kappa. Consistency of the mixture was 10 %, treatment temperature 60 °C and duration of treatment 90 min. After the alkali treatment the pulp was washed in the same way as after the oxidation phase.

After this, the bleaching was continued by repeating the oxidation and alkali phases and then once more the oxidation phase and washing the pulp between these phases as described above. For the combined wash waters, the amount of organically bound chlorine (AOX) and the chemical oxygen demand (COD) were determined, and these are presented in Table 1 (experiment 3) below.

In addition to the above-described experiment (exp. 3) illustrating the invention, two reference experiments (experiments 1 and 2) and an additional experiment (exp. 4) were carried out, and the AOX and COD values of the combined wash waters obtained from different stages of the experiments are also presented in Table 1. The experiments were performed as follows:

Experiment 2 (reference): No enzyme treatment was employed. The dosage of bleaching chemicals in different stages of treatment during the bleaching was 2 x kappa, the commonly used dosage. In other respects, the experiment was analogous to that described above (exp. 3).

Experiment 1 (reference): No enzyme treatment was employed. The bleaching chemical used in the oxidation stages was pure chlorine gas, in a dosage of 2 x kappa. In other respects, the experiment was analogous to that described above (exp. 3.)

Experiment 4: The pulp was treated with an enzyme and bleached as described above (exp. 3). In addition, the pulp was washed after the enzyme treatment, before the first oxidating treatment, with a mixture of chlorine dioxide and chlorine gas. The present invention comprises a procedure employing the principle of this experiment.

TABLE 1

Bleaching	AOX (kg/t of chemical pulp)	COD
Experiment 1 (reference) No enzyme treatment Cl_2 bleaching	2.6	58.1
Experiment 2 (reference) No enzyme treatment Bleaching with mixture 90 % ClO_2 + 10 % Cl_2	1.0	55.0
Experiment 3 Enzyme treatment Bleaching with mixture 90 % ClO_2 + 10 % Cl_2	0.6	40
Experiment 4 Enzyme treatment, washing Bleaching with mixture 90 % ClO_2 + 10 % Cl_2	0.6	40

The results indicate that, in comparison to corresponding bleaching without enzyme treatment, enzyme treatment combined with chlorine dioxide bleaching as provided by the invention substantially reduces the pollution load caused by the spent bleach liquors as measured in terms of AOX and COD values. Compared to the commonly used chlorine bleaching, the improvement achieved is even more distinct. Furthermore, it is worth noting that in the experiments representing the invention, the same degree of bleaching was achieved as in the reference experiments, which means that enzyme treatment has no adverse effect on the bleaching result.

Example 2

A diluted enzyme mixture (streptomyces hemicellulase) was added to 220 g of dry matter obtained from pine sulphate pulp (with a dry matter content of 30%) so that a mixture with a consistency of 10% and a xylanase activity of 5 U/g of pulp dry matter was obtained. The temperature in the enzyme treatment was 55 °C, the duration of treatment 2 h and pH 8.5.

After the enzyme treatment the pulp was washed in a Büchner funnel with a 20-fold amount of water.

After the washing, the pulp was subjected to an oxidating bleaching treatment using a mixture which contained 80 % chlorine dioxide and 20 % chlorine gas. The dosage of the mixture was 1.4 x kappa number of the pulp after enzyme treatment. Treatment temperature was 55 °C and duration of treatment 45 min. After the oxidating phase the pulp was washed in a Büchner funnel with a 20-fold amount of water.

Next, the pulp was subjected to an alkali treatment using a 5 % sodium hydroxide solution in a dosage of 0.9 x kappa. Consistency of the mixture was 2 %, treatment temperature 45-55 °C and duration of treatment 90 min. After the alkali treatment the pulp was washed in the same way as after the oxidation phase.

After this, the bleaching was continued by repeating the oxidation and alkali phases and then once more the oxidation phase and washing the pulp between these phases as described above. For the combined wash waters, the amount of organically bound chlorine (AOX) and the chemical oxygen demand (COD) were determined, and these are presented in Table 2 (experiment 4) below.

In addition to the above-described experiment (exp. 4) illustrating the invention, three reference experiments (experiments 1-3) were carried out, and the AOX and COD values of the combined wash waters obtained from different stages of the experiments are also presented in Table 2. The experiments were performed as follows:

Experiment 3: No enzyme treatment was employed. The dosage of bleaching chemicals in different phases of treatment during the bleaching was 2 x kappa, the commonly used dosage. In other respects, the experiment was analogous to that described above (exp. 4).

Experiment 2: The pulp was treated with an enzyme as described above. The bleaching chemical used in the oxidation phases was pure chlorine gas, in a dosage of 2 x kappa. In other respects, the experiment was analogous to that described above (exp. 4.)

Experiment 1: No enzyme treatment was employed. The bleaching chemical used in the oxidation phases was pure chlorine gas, in a dosage of 2 x kappa. In other respects, the experiment was analogous to that described above (exp. 4.)

TABLE 2

Bleaching	AOX (kg/t of chemical pulp)	COD
Experiment 1 (reference) No enzyme treatment Cl_2 bleaching	4.0	71
Experiment 2 (reference) Enzyme treatment, washing Cl_2 bleaching	2.9	63
Experiment 3 No enzyme treatment bleaching with mixture 80 % ClO_2 + 20 % Cl_2	1.7	44
Experiment 4 Enzyme treatment, washing Bleaching with mixture 80 % ClO_2 + 20 % Cl_2	1.0	36

The results indicate that, in comparison to corresponding bleaching without enzyme treatment, enzyme treatment combined with chlorine dioxide bleaching as provided by the invention substantially reduces the pollution load caused by the spent bleach liquors as measured in terms of AOX and COD values. Compared to the commonly used chlorine bleaching, the improvement achieved is even more pronounced. It can also be seen that when used in conjunction with chlorine dioxide bleaching, enzyme treatment produces a much more distinct improvement than when used in conjunction with the conventional chlorine dioxide bleaching. It should be noted that in this case, too, the same degree of bleaching of the pulp was achieved in the experiment representing the invention as in the reference experiments, which means that enzyme treatment had no adverse effect on the bleaching result.

It is obvious to a person skilled in the art that different embodiments of the invention are not restricted to the examples described above, but that they may instead be varied within the scope of the following claims. For example, in the alkali treatment stages phases of the bleaching process, oxygen may be present in addition to the alkali, and the duration of the enzyme treatment may vary from a few minutes to several hours (e.g. 5 min. - 10 h).

Claims

1. Procedure for the bleaching of pulp, in which procedure an oxidating bleaching chemical containing chlorine is used, **characterized** in that, in the oxidation stage, a chemical with a chlorine dioxide content of at least 70 % is used, that the pulp is subjected to enzyme treatment before the oxidation, and that, after the oxidation and enzyme treatment, the pulp is treated with an alkali

2. Procedure according to claim 1, **characterized** in that the bleaching chemical used in the oxidation stage is a mixture containing chlorine gas in addition to chlorine dioxide.

3. Procedure according to any one of the preceding claims, **characterized** in that the pulp is treated with an enzyme and washed before the first oxidation stage.

4. Procedure according to any one of the preceding claims, **characterized** in that, after the oxidation stage, the pulp is washed, whereupon the bleaching process continues with an alkali treatment.

5. Procedure according to any one of the preceding claims, **characterized** in that the enzyme treatment is carried out in a temperature range of 10-90 °C, preferably 40-75 °C, with pH values in the range 3.0-10.0, preferably 4.0-9.0.

6. Procedure according to any one of the preceding claims, **characterized** in that the enzyme used is a hemicellulase, cellulase, pectinase esterase or a mixture thereof.

Patentansprüche

1. Verfahren zum Bleichen von Zellstoff, wobei ein oxidierendes Bleichmittel, welches Chlor enthält, verwendet wird, dadurch gekennzeichnet, daß in der Oxidationsstufe eine Chemikalie mit einem Chlordioxid-Gehalt von wenigstens 70 % verwendet wird, daß der Zellstoff einer Enzym-Behandlung vor der Oxidation unterworfen wird, und daß der Zellstoff nach der Oxidations- und Enzym-Behandlung mit einem Alkali behandelt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das in der Oxidationsstufe angewandte Bleichmittel ein Gemisch ist, das zusätzlich zum Chlordioxid Chlorgas enthält.

3. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß der Zellstoff vor der ersten Oxidationsstufe mit einem Enzym gebleicht und gewaschen wird.

4. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß der Zellstoff nach der Oxidationsstufe gewaschen wird, worauf der Bleichprozeß mit einer Alkali-Behandlung fortgesetzt wird.

5. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß die Enzym-Behandlung in einem Temperaturbereich von 10-90 °C, am besten 40-75 °C bei p_H-Werten im Bereich

von 3,0 - 10,0, am besten 4,0 - 9,0 durchgeführt wird.

6. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß das angewandte Enzym eine Hemicellulase, eine Cellulase, eine Pectinase, eine Esterase oder ein Gemisch hieraus ist.

Revendications

1. Procédé de blanchiment de pâte, dans lequel on utilise un produit chimique de blanchiment oxydant contenant du chlore, caractérisé en ce que, dans l'étape d'oxydation, on utilise un produit chimique présentant une teneur en dioxyde de chlore d'au moins 70 %, en ce que la pâte est soumise à un traitement par une enzyme avant l'oxydation, et en ce que, après l'oxydation et le traitement à l'enzyme, la pâte est traitée par un alcali.

2. Procédé selon la revendication 1, caractérisé en ce que le produit chimique de blanchiment utilisé dans l'étape d'oxydation, est un mélange contenant du chlore gazeux en plus du dioxyde de chlore.

3. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la pâte est traitée par une enzyme et lavée avant la première étape d'oxydation.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que, après l'étape d'oxydation, la pâte est lavée puis le processus de blanchiment se poursuit par un traitement à l'alcali.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le traitement à l'enzyme est effectué dans une plage de températures de 10 à 90 °C, et de préférence de 40 à 75 °C, avec des valeurs de pH se situant dans la plage de 3,0 à 10,0 et de préférence de 4,0 à 9,0.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'enzyme utilisée est une hémicellulase, une cellulase, une pectinase, une estérase, ou un mélange de ces produits.